THE BEHAVIOR OF MANGANESE IN THE SOIL AND THE MANGANESE CYCLE

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

JUNE 1947

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AN ACKNOWLEDGMENT

The author wishes to express his most sincere appreciation and thanks to Dr. J. H. Beaumont and the Hawaii Agricultural Experiment Station for the use of its greenhouse and the conveniences in the Department of Agricultural Chemistry and Soils. The availability of these facilities has made possible the conducting of this research problem. The author also wishes to extend his most sincere appreciation to Dr. G. Donald Sherman for his kindly encouragement, and his continuous counsel and advice.

INTRODUCTION

Many of the soils in Hawaii which are utilized for agricultural purposes are characterized by a high manganese content. This high manganese content is particularly marked in the red residual soils which comprise a major portion of Hawaiian soils. Most of these soils have a total manganese content ranging from 1 to 4 percent, which is considered extremely high. Wilcox and Kelley (43)[1] in their work with manganiferous soils gave analyses ranging from as high as 4.43 to 9.74 percent Mn_3O_4. While it is true that the total analysis of manganese in the soil is not a measure of availability to plants, it is generally accepted that a certain portion of the total is potentially available and may play a role in the nutrition of plants. If it is remembered that a total manganese content of greater than 0.25 percent is considered high in the United States, then the magnitude of the manganese problem in Hawaii becomes apparent.

Many of the crops grown in Hawaii apparently are not affected by the high manganese content in the soil. Sugar cane, the major crop of Hawaii, and grasses in general seem to thrive on these soils and do not seem to be affected in any adverse manner. The growers of pineapple, however, experienced some difficulties with the manganese problem. When pineapples were grown on the highly manganiferous soils,

1. Figures in parenthesis refer to "Literature Cited."

the yields were low and the general appearance of the plants was poor. The earlier investigators believed that the high concentration of manganese in the soil was toxic to the growth of pineapples. According to Johnson (16) the problem is not a direct manganese toxicity, but more a manganese induced iron deficiency, which brought about a chlorosis of the pineapple plant. This problem has been solved by the periodic spraying of the pineapple plants with iron sulfate solution. No report on the effects of excess manganese on the growth of other crops in Hawaii has been published. However, some of the workers at the Hawaii Agricultural Experiment Station have indicated (personal discussion) that manganese may be toxic to the growth or may limit the growth of many agricultural truck crops. It has also been the experience of the writer to encounter difficulties in the growing of legumes and other crops in the manganiferous soils.

Although a number of workers have investigated and analyzed the total and available (acid and water soluble) manganese in soils, very little work has been done on how to control or influence the available manganese in Hawaiian soils. In this study an attempt will be made to determine the soil treatments and soil conditions which would make manganese either more available or less available. In Hawaii, because of the large amounts of manganese in the soil, the manganese problem would logically center on the question of making manganese less available. It is therefore the purpose of this study to determine the various factors which influence the availability of manganese with the aim of controlling or at least influencing the availability of manganese in the soil.

HISTORICAL REVIEW

In recent years much work has been done by a number of workers to determine whether manganese is an essential element in the nutrition of plants. Each investigator has added to the knowledge and understanding of the role of manganese in plant nutrition. Much evidence has been presented showing that manganese plays an essential part in the metabolism of plants. Today manganese is universally accepted as necessary for the growth of plants. A summary of the works of the numerous investigators in establishing the necessity of manganese in plant nutrition will not be given since a number of summaries (37, 29) are available which cover the subject much more comprehensively and adequately than can be accomplished in this study.

Although it has been definitely established that manganese is an essential element in the nutrition of plants, many workers have shown that manganese when present in large amounts in the available form can be toxic to the growth of plants. A brief review of this phase of the manganese investigation will be given since no review is available, and since manganese excess is one of the soil problems in Hawaii.

In 1909, Kelley (17) reported that some of the pineapple soils of Hawaii contain black spots on which pineapples turn yellow and do not grow successfully. He attributed the poor growth of pineapples to the high amounts of manganese in the black spots. Later in 1912, Wilcox and Kelley (43) described the physiological difficulties in the pineapple plants arising from an excess of manganese in the soil. They state, "The most conspicuous effect of manganese on this plant is seen in the bleaching of the chlorophyll which first begins to fade, the chloroplasts lose their organized structure, and later the color disappears altogether." These workers, however, were not able at that time to offer any corrective measures for the manganiferous soils.

In 1916 Johnson (15) showed that the toxic effect of manganese was actually a reduction in the assimilation of iron caused by an excess of manganese. He also showed that when plants growing on manganiferous soils were sprayed with ferrous sulfate solution, the plants grew normally. Eight years later, after further experimentation, Johnson (16) was able to confirm his findings with more experimental data. He came to the conclusion that manganese toxicity is actually a depression in the assimilation of iron in the plant.

Funchess (4) in his studies on nitrification in 1918 described a peculiar occurrence that took place when dried blood was applied to the soil in the autumn and covered with a mulch during the winter. When the mulch was removed in the spring a brown crust had formed. Upon analysis this brown crust showed a high concentration of soluble manganese. Plants grown on this brown crust became sickly and soon died. Funchess attributed the infertility of this soil to the presence of manganese in the soil solution, rather than to toxic organic bodies. A year later, Funchess (5) was able to present more confirmatory evidence supporting his previous findings; however, he was of the opinion that actual acidity as well as soluble manganese in the soil solution, was responsible for the toxicity found in soils fertilized with dried blood.

In the tobacco investigations that Jacobson and Swanback (13) conducted, they showed that excessive amounts of manganese were responsible for some of the difficulties encountered in the growing of tobacco. In another study Jacobson and Swanback (14) reported that with increased acidity of the soil, the plant intake of manganese was increased. Bortner (2) in his work with Turkish tobacco in Kentucky noted a chlorotic condition in tobacco. He attributed this chlorotic condition to an excess of manganese in the soil. McCool (27) showed that if large amounts of manganese were applied to the soil or if the soil was steam-heated, plants grown on these soils developed chlorotic symptoms. He demonstrated that steam-heating of soil released large amounts of available manganese. In the work at Connecticut, LeCompte (19) reported that "black leaf tobacco" may be caused by high amounts of manganese.

More recently, Somers and Shive (39) in their work with soybean reported that symptoms of iron toxicity corresponded to those of manganese deficiency, and symptoms of manganese toxicity corresponded to those of iron deficiency. They proposed that when there is an excess of manganese, the plant apparently suffers from iron deficiency, and vice versa. They concluded that it is the ratio of iron and manganese in the plant and in the external medium that is of prime importance and not the absolute concentrations--within certain limits--of iron and manganese. Hopkins, et al. (12) confirm the findings of Somers and Shive (39). They also state that manganese toxicity exists in Puerto Rico, and that chlorosis, necrosis, sunscald, and decreased growth are associated with excess manganese.

The works of these investigators indicate conclusively that manganese is an essential element in plant nutrition, and also that manganese, when present in large amounts, may be toxic to the growth of plants. In areas where manganese is deficient in the soil, the problem can be solved either by making the manganese more available, or by the relatively simple procedure of applying soluble manganese compounds to the soil or to the plant. In Hawaii the problem is an excess of manganese in the soil, which is a problem that cannot be readily solved. For the solution of this problem an understanding of the behavior of manganese in the soil under varying soil conditions is necessary. A number of workers have studied various phases of this problem, and a brief review of this subject will be given.

In 1913, Kelley and McGeorge (18) showed that heating the soil at 100°C. and 250°C. increased the water soluble manganese in the soil. Funchess (4) in 1918 showed that dried blood applied to the soil increased the soluble manganese in the soil. He further showed that liming seemed to counteract the toxic effect of excess manganese. McHargue (28) in his work with acid and neutral soils showed that manganese when applied to acid soils was toxic, but when applied to neutral soils was beneficial. He showed that lime tended to neutralize the toxic effect of excess manganese. Gilbert, et al. (9) reported that liming heavily with calcium or magnesium carbonate caused a chlorosis to appear in the crops. They attributed this chlorosis to manganese deficiency.

Lee and McHargue (20), working with a disease of sugar cane called "Pahala Blight" on a soil from the Island of Hawaii, showed that this disease, which resulted in a chlorosis of the plant, was actually caused by a deficiency of manganese. They also indicated that this disease occurred only on neutral and alkaline soils. Willis (45) in his work with the Coastal Plain soils also reported that liming caused the plants to show symptoms of manganese deficiency. He also stated that heavy applications of calcium phosphate can bring about manganese deficiency. In the analytical work conducted in the laboratory, Mann (25) was able to show that liming decreased the solubility of manganese in the soil. He was also successful in showing that there was positive correlation between his laboratory findings and crop work in the field. Snider (38) reported that liming reduced the availability of manganese. He further reported that superphosphate and rock phosphate increased the uptake of manganese by plants. In work in the greenhouse, Albrecht and Smith (1) demonstrated that when lime was mixed throughout the soil in pots, the uptake of manganese by plants was decreased; however, when the lime was applied only on the surface portion of the soil, the manganese uptake by plants was increased. They also showed that phosphorus when applied to the soil increased the uptake of manganese.

Piper (34) in 1931, after a thorough investigation of manganese in the soil, presented a number of observations and conclusions, which have contributed greatly to the understanding of the manganese problem in soils. He showed that when soils were water-logged, manganese was released. He further showed that when soils were stored at 45 percent water saturation no soluble manganese was present, but when soils were stored at 90 percent water saturation manganese was released. When 0.25 percent dextrose was added to the soil and saturated with water, greater amounts of manganese were released. He demonstrated that with increasing pH, the amount of manganese absorbed by Algerian oats was decreased. He showed that when Algerian oats grown on alkaline soils were watered to 45, 60, and 75 percent water saturation, the plants suffered from manganese deficiency. However, when the plants were watered to 90 percent water saturation the plants grew normally.

Conner (3) in 1932 showed that addition of hydrochloric acid or acid residual fertilizers (ammonium nitrate, ammonium sulfate, urea, etc.) made manganese more available. He showed that basic soil additions or basic residual fertilizers (sodium nitrate, calcium carbonate, etc.) decreased the availability of manganese. Conner also demonstrated that steam-heating of soils made manganese more available. McCool (27) found that water-soluble manganese was lowest in the spring and after heavy precipitation in the autumn, The maximum amounts of manganese were found near the surface in August and in the soils that contained decaying sod. Temperature was listed by McCool as one of the reasons for the changes in the manganese level. He found that water-logging, steam-heating, and addition of acid residual fertilizers increased the amount of water-soluble manganese. Addition of lime in his work reduced the amount of manganese.

Steenbjerg (40) added quinone, quinhydrone, sodium sulphite, metol (agfa), formaldehyde, and potato starch to soils, and found that these treatments gave partial or complete control of manganese deficiency. Water-logging and addition of saccharose, when done separately, failed to alleviate manganese deficiency, but when the two treatments were done simultaneously control of manganese deficiency was effected. Harmer (10), in his work with unproductive organic soils, showed that manganese deficiency caused by calcium and other minerals can be corrected by applications of sulfur or manganous sulfate or both. Wain, et al. (41) presented data showing that water-logging and steam-sterilization increased the amount of manganese extracted by ammonium acetate solution.

Sherman, et al. (36) conducted some work on the influence of halides on the oxidation of manganese in soils. They showed that iodides retarded the oxidation of manganese in alkaline soils, and that in acid soils manganese was reduced chemically with the liberation of iodine. Fluorides increased the capacity of the soil to oxidize manganese. Bromides increased the oxidation of manganese in alkaline soils, but their action in acid soils was uncertain. Light applications of chlorides had no effect on the manganese. Heavy applications increased the exchangeable manganese.

Recently in Hawaii, Fujimoto and Sherman (6) showed that drying, heating, and steam-sterilization increased the exchangeable manganese in Hawaiian soils to an extraordinarily high degree. They also showed that wetting the soil to approximately the moisture content at maximum field capacity reduced the exchangeable manganese. They suggested that the fixation and release of manganese may take place by the hydration or dehydration of a complex, hydrated manganese oxide of the following type:

$$(MnO)_x(MnO_2)_y(H_2O)_z$$

The postulate contends that when the water of hydration is split off, the rest of the molecule becomes unstable, thus creating the conditions for the solution of a certain portion of the original molecule, specifically the manganous oxide. They suggest also that this hydration and dehydration mechanism may be a reversible process.

The discussion of the behavior of manganese in soils thus far has been confined to the chemical and agronomic aspects. There is another group of investigators who feel that microbiological activity in the soil plays a major role in the availability of manganese in the soil.

Gerretsen (7) in 1935 showed that sterilization of manganese deficient soils with formalin corrected the deficiency. Reinfection of the sterilized soil with unsterilized soil caused the reappearance of the deficiency symptoms in their original intensity. He concluded that bacteria precipitated manganese as the dioxide and made the soil deficient in manganese. Later, Gerretsen (8) isolated the bacteria by a technique he developed. In 1940, Leeper and Swaby (22) used Gerretsen's method of biological oxidation of manganese, and found that the oxidation could take place in the pH limits of 4.8 to 8.9; whereas, Gerretsen stated that the biological activity takes place only between the pH limits of 6.3 to 7.8 with maximum at pH 7.

MacLachlan (24) duplicated the technique of Gerretsen for the isolation of manganese-precipitating bacteria. He was successful in isolating the bacteria, and identified the bacteria as gram negative medium-sized rods. Mann and Quastel (26) concluded that since such diverse cell poisons as chloretone, sodium iodo acetate, and sodium azide brought about a marked inhibition in the rate of formation of higher oxides of manganese in soil, almost all oxidation in soils is accomplished by biological means.

If the findings of all the workers cited in this study on the behavior of manganese are compiled and classified, the following classification, based upon physical, chemical, and biological changes in the soil, seems to be the most logical:

1. Effect of physical changes
    a. Changes in temperature
        1. Heating releases manganese.
        2. Steam-sterilization releases manganese.
    b. Changes in water saturation
        1. Water-logging releases manganese.
        2. Wetting of soils (but not water-logging) fixes manganese.
        3. Drying releases manganese.
2. Effect of chemical changes
    a. Changes in pH
        1. Increase in pH fixes manganese.
        2. Reduction in pH releases manganese.
        3. Addition of acids and acid residual fertilizers releases manganese.
        4. Addition of alkali and basic residual fertilizers fixes manganese.
        5. Addition of sulfur releases manganese.
    b. Changes in oxidation-reduction conditions
        1. Addition of reducing agents (quinone, quinhydrone, sodium sulphite, formaldehyde, starch, sugar, etc.) releases manganese.

c. Addition of halides

1. Addition of iodides releases manganese.

2. Addition of fluorides fixes manganese.

3. Addition of bromides fixes manganese in alkaline soils.

4. Addition of chlorides releases manganese when applied in large amounts.

d. Addition of phosphates

1. Sometimes manganese is fixed and sometimes released (results are conflicting).

3. Effect of biological activity

a. Bacterial activity fixes manganese.

This classification of the results of investigations may serve to give a clearer comprehension of the study of manganese behavior to date. In this study some of the procedures of previous workers will be utilized and other lines of research will be developed.

EXPERIMENTAL PROCEDURE

For the major part of this study, soil from the Poamoho sub-station of the Hawaii Agricultural Experiment Station was used. This soil was used because of its high manganese content, which would make the changes in the manganese level quite evident. At a later stage in the experimentation, soils from Manoa, Aiea, and Koko Head were used. The Manoa soil was taken from a vegetable crop field at the University of Hawaii. It is medium in manganese content. The Aiea soil was taken from a sugar cane field in Aiea. It is high in manganese. The Koko Head soil was taken from a farm located at Koko Head. It is medium in manganese content.

The analytical method used in the determination of manganese was essentially the same as the colorimetric method of Willard and Greathouse (44), with modifications by Fujimoto and Sherman (6). The color of the manganese solution was read with a photoelectric colorimeter with a green filter which had a transmission range of 500 to 570 millimicron wave length of light with maximum transmission at 530 millimicron.

To determine the effects of the various soil treatments upon the availability of manganese, the soils were initially treated with various substances, moistened to approximately the moisture content at maximum field capacity, and allowed to stand in the laboratory for two weeks. After the two week period had elapsed, the exchangeable manganese was extracted with normal ammonium acetate solution adjusted to pH 6.8. In the treatments that fixation of manganese was expected, the soils were initially oven-dried to increase the exchangeable manganese to a high level so that any decrease in the level of exchangeable manganese would be of a greater magnitude than would be expected if an unheated soil were used. In the treatments that release of manganese was expected, unheated soil was used.

During the latter part of the investigation, it was considered desirable to obtain some evidence of the chemical or physical reactions of manganese in the soil. To do this, the soil was treated with a number of reducing agents, wetted to the moisture content at maximum field capacity, and extracted with ammonium acetate solution. Following this the extracted soil was oven-dried at 105°C. for twenty-four hours and reextracted with ammonium acetate solution. This was done in order to see whether the hydration-dehydration hypothesis of Fujimoto and Sherman (6) could be verified or confirmed.

Most of the laboratory chemical treatments were also duplicated in the greenhouse. The soils were given the various treatments, placed in pots, and cowpeas were grown in them. The equivalent of five hundred pounds per acre of fertilizer (7-14-14) was added to each pot. Cowpea was used in this study because of its rapid growth and relatively simple germination. After a short period of growth the plants were harvested, dried, and weighed. The dried plant parts were then ground and analyzed for total manganese. Four cowpeas were grown in each pot, and each treatment had four replicates. The yields are presented but no attempt to interpret the yield data is made, for the sole purpose of the growing of the plants was to determine whether there was any correlation between plant uptake of manganese and laboratory findings of release or fixation of manganese.

The description of the procedure given in this section is rather general. However, a more detailed description of the experimental procedure will be given wherever necessary.

The following soil treatments were used in this study:

1. Lime ($CaCO_3$)
2. Dolomite ($CaCO_3.MgCO_3$)
3. Sulfur (S)
4. Organic matter (sugar, sugar cane, and pineapple leaves)
5. Reducing agents (hydroquinone, hydrazine sulfate, etc.)

EXPERIMENTAL RESULTS

Effect of lime ($CaCO_3$) and dolomite ($CaCO_3.MgCO_3$) on the fixation of manganese in soils.

In order to determine the effect of lime and dolomite on the fixation of manganese, the soil was heated at 100°C. for twenty-four hours and cooled. Incremental amounts of lime and dolomite ranging from no treatment up to thirty-two tons per acre were applied. The soils were wetted and stored in the laboratory for two weeks. Exchangeable manganese was extracted and determined. The results for the lime treatment are shown in Table I, and the results for the dolomite treatment are shown in Table II.

Table I. The effect of rates of application of lime to Poamoho soil on the fixation of manganese

Amount of lime per acre	Exchangeable manganese p.p.m.	Manganese fixed over check p.p.m.
None	1605	----
500 lbs.	1576	29
1000 lbs.	1461	144
1 ton	1368	237
2 tons	1195	410
4 tons	969	636
8 tons	656	949
16 tons	362	1233
32 tons	148	1457

Table II. The effect of rates of application of dolomite to Poamoho soil on the fixation of manganese

Amount of dolomite per acre	Exchangeable manganese p.p.m.	Manganese fixed over check p.p.m.
None	1659	----
500 lbs.	1659	0
1000 lbs.	1678	-19
1 ton	1670	-11
2 tons	1678	-19
4 tons	1596	63
8 tons	1536	123
16 tons	1376	283
32 tons	1324	335

When lime is applied to the soil, exchangeable manganese decreases rapidly with increasing applications of lime. Dolomite seems to have the same effect as lime, but its action is not as great as lime. The results for dolomite are a little erratic, but the general tendency seems to be toward decrease in exchangeable manganese with increase in dolomite application. The dolomite used in this study was very coarse. This coarseness may explain the weak action of dolomite in this study. The lime used in this study was commercially reprecipitated, "chemically pure" calcium carbonate. The lime was in a finely subdivided state.

In the greenhouse work, lime and dolomite were applied in increasing amounts from no treatment to eight tons of lime or dolomite. Each treatment had four replicates. Four cowpea seedlings were planted in each pot. The plants were grown for twenty days, and all the above-ground parts were harvested. The plants were dried, weighed, and analyzed for total manganese. The results for the lime and dolomite treatments are given in Table III and IV.

When lime or dolomite are applied to the soil the uptake of manganese by plants is decreased. This result confirms the findings in the soil analysis work. Generally, it seems that lime and dolomite are just as effective in reducing the uptake of manganese by plants. It is interesting to note that the first light application of five hundred pounds per acre of either lime or dolomite reduces the uptake

Table III. The effect of rates of application of lime to Poamoho soil on the yield and manganese content of cowpeas.

Tons lime per acre	Average yield of four replicates, grams	Manganese content p.p.m.	Decrease in manganese uptake as compared to check, p.p.m.
0.0	2.5	1110	---
0.5	1.4	665	445
1.0	2.8	530	580
2.0	2.1	425	685
4.0	2.0	255	855
8.0	2.2	265	845

Table IV. The effect of rates of application of dolomite to Poamoho soil on the yield and manganese content of cowpeas.

Tons dolomite per acre	Average yield of four replicates, grams	Manganese content p.p.m.	Decrease in manganese uptake as compared to check, p.p.m.
0.0	2.5	1210	---
0.5	3.2	555	655
1.0	3.4	650	560
2.0	2.9	605	605
4.0	2.2	330	880
8.0	2.6	210	1000

of manganese tremendously. With further increase in application, the manganese uptake is reduced gradually.

Effect of sulfur on the release of manganese in soils

Sulfur was added to the Poamoho soil in increasing amounts from none to four tons per acre. The soil was moistened, and was allowed to stand in the laboratory for two weeks. The exchangeable bases were extracted from the soil, and manganese was determined in the extract. The results from this study are presented in Table V.

Table V. The effect of rates of application of sulfur to Poamoho soil on the release of manganese

Sulfur tons per acre	Exchangeable manganese p.p.m.	Manganese released over check p.p.m.
0.0	7.8	---
0.5	12.4	4.6
1.0	16.2	8.4
2.0	29.1	21.3
4.0	39.9	32.1

The results show that when sulfur is added to soils, manganese is released or made more available. This study was also extended to greenhouse work. The results are shown in Table VI.

Although the increase in exchangeable manganese by the application of sulfur as shown in Table V is not marked, the increase in plant uptake of manganese by the addition of sulfur to the soil is surprisingly great. In both the laboratory study and the greenhouse work, the level of manganese is increased by the addition of sulfur to the soil.

Table VI. The effect of rates of application of sulfur to Poamoho soil on the yield and manganese content of cowpeas

Sulfur tons per acre	Average yield of four replicates, grams	Manganese content p.p.m.	Increase in manganese uptake over check, p.p.m.
0.0	3.3	1320	----
0.5	2.6	2620	1300
1.0	2.2	3250	1930
2.0	2.3	6940	5620
4.0	1.6	9000	7680
8.0	1.4	9000	7680

Effect of organic matter on the release of manganese in soils

Organic matter as used in this study does not refer to the active soil organic matter or humus which some workers have characterized as a protein-lignin complex, or others as black-pigments of soils. The term organic matter as used in this study refers to any organic substance, mixtures of substances, or plant parts. The organic matter used in this study is characterized by a high carbon-nitrogen ratio, which when placed in soils would increase the biological activity in the soil.

Sugar (sucrose), ground pineapple leaves, and ground sugar cane leaves were used in this study. Sugar, since it contains no nitrogen, has a carbon-nitrogen ratio of positive infinity. Pineapple and sugar cane leaves have a very high carbon-nitrogen ratio. Sugar was added to the soil in incremental amounts, and the soil was moistened and allowed to stand in the laboratory for one week. The results after analysis are shown in Table VII. Pineapple leaves and sugar cane leaves were added to the soil and were given the same treatments. The soils were sampled at intervals and manganese analyses were performed. The amounts of pineapple and sugar cane leaves applied to the soil were extremely high in some cases. This was done because the plant residues left in the field after certain crops are harvested are high. In the case of pineapples, it has been estimated by some workers that the above-ground residual parts may be as high as two hundred tons per acre. Table VIII gives the results of the pineapple leaves application, and Table IX gives the results of the sugar cane leaves application.

Table VII. The effect of rates of application of sugar to Poamoho soil on the release of manganese

Tons sugar per acre	Exchangeable manganese p.p.m.	Manganese released over check p.p.m.
0.0	5.1	----
0.5	6.1	1.0
1.0	6.3	1.2
2.0	7.3	2.2
4.0	135.9	130.8
8.0	118.6	113.5
16.0	466.7	461.6

Table VIII. The effect of rates of application of pineapple leaves to Poamoho soil on the release of manganese

Pineapple leaves tons per acre	Exchangeable manganese, parts per million		
	1st day	7th day	19th day
0	37.8	16.6	6.5
1	43.0	22.5	7.3
2	51.7	35.7	7.3
4	73.7	53.6	54.8
8	119.3	164.8	1828.6
16	203.1	152.2	192.8
32	307.1	1936.0	2801.3
64	437.6	2596.2	3078.3
128	586.7	3526.5	3593.8
256	765.1	924.9	3102.9

Table IX. The effect of rates of application of sugar cane leaves to Poamoho soil on the release of manganese

Sugar cane leaves tons per acre	Exchangeable manganese, parts per million		
	1st day	7th day	19th day
0	38.5	30.4	3.7
1	40.6	34.6	6.7
2	46.8	47.3	18.3
4	52.8	85.3	19.3
8	59.0	811.2	308.6
16	112.9	114.4	78.0
32	165.5	217.7	445.8
64	349.1	951.3	2853.3
128	415.0	1507.1	4693.3
256	550.9	666.7	3342.2

Table VII, VIII, and IX clearly show that with increasing applications of sugar, pineapple leaves, or sugar cane leaves, the level of exchangeable manganese gradually increases. With the pineapple and sugar cane leaves three separate determinations were performed at different intervals of time. It is seen that the release of manganese takes place very rapidly, for the release of manganese is evident after twenty-four hours. With further standing, the level of exchangeable manganese increases to extremely high levels in the higher applications of organic matter. In the lower treatments of pineapple and sugar cane leaves, the level of exchangeable manganese increases and then gradually decreases. The same behavior would probably be true for the higher applications, if the experiments were carried out for longer periods.

Table X shows the amount of manganese uptake by cowpeas when sugar cane leaves were added to the soil. This experiment was carried out in a manner similar to the previous pot experiments.

Sugar cane leaves when added to soils increase the manganese uptake by cowpeas. It seems logical to assume that pineapple leaves and sugar would have the same effect on manganese uptake by plants as sugar cane leaves; therefore, no pot experiments were performed for both pineapple leaves and sugar.

Table X. The effect of rates of application of sugar cane leaves to Poamoho soil on the yield and manganese content of cowpeas

Sugar cane leaves tons per acre	Average yield of four replicates grams	Manganese content p.p.m.	Increase in manganese uptake over check, p.p.m.
0	2.5	960	----
1	2.2	1240	280
2	2.5	1150	190
4	2.3	1260	300
8	1.8	1625	665
16	1.5	1550	590
32	1.5	1800	840
64	1.0	3130	2170

Effect of reducing agents

The soil treatments up to this point were those that are normally used in agricultural practices. It seems necessary to use other treatments that are not ordinarily used in agricultural practices and some that are agriculturally not feasible, for the further understanding of the manganese question. In this series of experiments various reducing agents were used. The reducing agents included hydroquinone, stannous chloride, formaldehyde, hydrazine sulfate, and potassium iodide. Pineapple leaves were also included in this study, because the actual action of any organic matter with a high carbon-nitrogen ratio is one of reduction.

The soils were treated with the various reducing agents, moistened to approximately the moisture content at maximum field capacity, and stored for three weeks. The soils were mixed at intervals, and water was added at intervals to maintain the initial moisture content. The exchangeable manganese in the soil was extracted with ammonium acetate solution and analyzed. The extracted soil was then placed in the oven and heated at 105°C. for twenty-four hours. Following this, the soil was again extracted with ammonium acetate solution. The second extraction was also analyzed for manganese. The second extraction after heating was performed to determine whether there would be any increase in the hydrated forms of manganese oxide that Fujimoto and Sherman (6) propose. This set of experiments was performed on four different soils. The soils used were the Poamoho soil, the Aiea soil, the Koko Head soil, and the Manoa soil. One hundred grams of soil were used in each treatment. The results are given in Tables XI, XII, XIII, and XIV.

It is seen in all four soils that the addition of a reducing agent increased the amount of exchangeable manganese. Increase in the hydrated form takes place in every treatment in every soil, except in one treatment in the Poamoho soil. There is an increase in the total amount of manganese extracted by the addition of reducing agents.

Table XI. Effect of reducing agents on soil manganese (Poamoho Soil)

Treatment	Exchangeable manganese p.p.m.	Exchangeable Mn after heating* p.p.m.	Total extracted manganese p.p.m.	Increase in exchangeable Mn over check p.p.m.	Increase in hydrated form p.p.m.	Increase in total Mn extracted over check. p.p.m.
None	11.0	2794.1	2805.1	--	--	--
0.5 gm. Hydroquinone	1806.2	3356.6	5162.8	1795.2	562.5	2357.7
0.5 gm. Stannous Chloride	266.7	2945.7	3212.4	255.7	151.6	407.3
0.5 gm. Formaldehyde	2516.1	3225.8	5741.9	2505.1	431.7	2936.8
0.5 gm. Hydrazine Sulfate	3361.3	2621.8	5983.1	3350.3	-172.3	3178.0
0.5 gm. Potassium Iodide	457.8	2882.4	3340.2	446.8	88.3	535.1
10 gm. Pineapple Leaves	2019.2	3865.4	5884.6	2008.2	1071.3	3079.5

* This is considered as the hydrated form which has become unstable with heating.

Table XII. Effect of reducing agents on soil manganese (Aiea Soil)

Treatment	Exchangeable manganese p.p.m.	Exchangeable Mn after heating* p.p.m.	Total extracted manganese p.p.m.	Increase in exchangeable Mn over check p.p.m.	Increase in hydrated form p.p.m.	Increase in total Mn extracted over check. p.p.m.
None	4.1	522.7	526.8	--	--	--
0.2 gm. Hydroquinone	225.8	727.7	953.5	221.7	205.0	426.7
0.5 gm. Stannous Chloride	9.7	648.4	658.1	5.6	125.7	131.3
0.5 gm. Formaldehyde	194.6	704.3	898.9	190.5	181.6	372.1
0.2 gm. Hydrazine Sulfate	92.1	817.2	909.3	88.0	294.5	382.5
0.2 gm. Potassium Iodide	13.5	572.8	586.3	9.4	50.1	59.5
5 gm. Pineapple Leaves	569.1	1270.7	1839.8	565.0	748.0	1313.0

* This is considered as the hydrated form which has become unstable with heating.

Table XIII. Effect of reducing agents on soil manganese (Koko Head Soil)

Treatment	Exchangeable manganese p.p.m.	Exchangeable Mn after heating* p.p.m.	Total extracted manganese p.p.m.	Increase in exchangeable Mn over check p.p.m.	Increase in hydrated form p.p.m.	Increase in total Mn extracted over check. p.p.m.
None	0.0	218.9	218.9	--	--	--
0.2 gm. Hydroquinone	313.8	281.3	595.1	313.8	62.4	376.2
0.5 gm. Stannous Chloride	2.0	237.2	239.2	2.0	18.3	20.3
0.5 gm. Formaldehyde	21.3	260.7	282.0	21.3	41.8	63.1
0.2 gm. Hydrazine Sulfate	5.2	398.5	403.7	5.2	179.6	184.8
0.2 gm. Potassium Iodide	14.1	295.0	309.1	14.1	76.1	90.2
5 gm. Pineapple Leaves	396.2	381.7	777.9	396.2	162.8	559.0

* This is considered as the hydrated form which has become unstable with heating.

Table XIV. Effect of reducing agents on soil manganese (Manoa Soil)

Treatment	Exchangeable manganese p.p.m.	Exchangeable Mn after heating* p.p.m.	Total extracted manganese p.p.m.	Increase in exchangeable Mn over check p.p.m.	Increase in hydrated form p.p.m.	Increase in total Mn extracted over check. p.p.m.
None	3.6	333.1	336.7	--	--	--
0.5 gm. Hydroquinone	698.0	421.8	1119.8	694.4	88.7	783.1
0.5 gm. Stannous Chloride	7.0	364.2	371.2	3.4	31.1	34.5
0.5 gm. formaldehyde	144.9	432.8	577.7	141.3	99.7	241.0
0.5 gm. Hydrazine Sulfate	444.0	460.0	904.0	440.4	126.9	576.3
0.5 gm. Potassium Iodide	125.0	436.8	561.8	121.4	103.7	225.1
10 gm. Pineapple Leaves	327.0	451.4	778.4	323.4	118.3	441.7

* This is considered as the hydrated form which has become unstable with heating.

DISCUSSION AND CONCLUSION

It was shown in the experimental results that the level of exchangeable manganese was decreased in the soil, and the amount of plant uptake of manganese was decreased by the application of lime and dolomite to the soil. It is believed by Sherman and Harmer (35), Leeper (23), and others that the fixation of manganese is brought about by the oxidation of manganous manganese to higher states of oxidation. Sherman and Harmer (35) also observed that neutral and alkaline conditions favor the formation of manganic manganese and acid conditions of manganous manganese.

When a manganous salt is dissolved in water, no oxidation of the manganous ion takes place and the solution remains stable indefinitely if no oxidizing agent is added to the solution. Oxygen in the air apparently does not oxidize the manganous ion in a water solution. The same holds true for an acidic solution of a manganous salt. Nichols and Walton (33) in their study of the autoxidation of manganous hydroxide added sodium hydroxide and other bases to a solution of a manganous salt and ammonium chloride. The ammonium chloride was present in the solution to prevent the precipitation of manganous hydroxide. They noticed that the oxidation of the manganous hydroxide by oxygen proceeded slowly at first and increased in reaction rate later when the higher oxides precipitated. They were able to establish that the presence of certain finely divided substances in the reacting medium accelerated the reaction rate. They attributed this to a surface catalytic effect. Mellor (30) in his comprehensive review shows that when a base is added to a solution of a manganous salt, manganous hydroxide forms as a white gelatinous precipitate. The fine state of subdivision of the manganous hydroxide favors its rapid oxidation to the hydrated dioxide form. The conclusions to be drawn from these studies are that the oxidation of the manganous ion by oxygen can take place in a basic medium and that the presence of certain finely divided substances will catalytically increase the rate of oxidation.

Lime and dolomite, when added to the soil, raise the pH of the soil, and bring about the conditions that favor the oxidation of manganese. The rate of oxidation proceeds rapidly because soil consists of finely divided particles. which will accelerate the rate of reaction. At the same time, lime and dolomite will increase the hydroxyl ion concentration to a point where the solubility product of manganous hydroxide is exceeded. When the solubility product is exceeded, manganous hydroxide precipitates in a finely divided state which will favor its rapid oxidation. In this way does fixation of manganese take place when lime or dolomite is added to the soil.

When sulfur was added to the soil, it was shown that the exchangeable manganese content was increased. It was shown also that the plant uptake of manganese was increased. Waksman (42) has shown that when sulfur is added to soils, the sulfur is rapidly oxidized principally by biological processes to sulfuric acid. The overall reaction is shown in the following chemical equation:

$$S_2 + 3\ O_2 + H_2O \rightleftharpoons 2\ H_2SO_4$$

Sulfuric acid would naturally lower the pH of the soil, and bring about the conditions for the reduction of the higher oxides of manganese as has been stated previously. The reduction of the higher oxides of manganese would make manganese more available in the soil.

It has been shown that the addition of organic matter with a high carbon-nitrogen ratio will increase the availability of manganese in soil. Organic matter with a high carbon-nitrogen ratio contains large amounts of easily oxidizable substances such as starch and sugar. When these substances are added to the soil in the form of residual plant parts, biological oxidation of the organic matter takes place with the formation of carbon dioxide. Leeper (23) states, "Biological reduction can take place at any pH value if the oxygen tension is low, when the anaerobic bacteria use the higher oxides as a source of oxygen." Reduction of the higher oxides takes place when the biological oxidation of organic matter proceeds at a rapid enough rate that the air cannot supply oxygen in adequate amounts. When this occurs, reduction of the higher oxides takes place to supply the needed oxygen. This leads to an increase in the available manganese.

The experimental results show that reducing agents increase the exchangeable manganese and the hydrated form of manganese. The reduction by the various reducing agents is a straightforward chemical reduction and shall not be discussed. The hypothesis of the hydrated form of manganese oxide and the release of available manganese by dehydration is a new concept, which was proposed by Fujimoto and Sherman (6) as a possible explanation for their experimental findings.

This postulate states that a certain portion of the manganese in the soil exists as a complex, hydrated oxide of the following type:

$$(MnO)_x(MnO_2)_y(H_2O)_z$$

When the water of hydration is split off, the rest of the molecule becomes unstable and breaks up into its component parts--the manganous oxide and the manganese dioxide. The manganous oxide then becomes available for absorption by plants. The reaction can be represented by the following chemical equation:

$$(MnO)_x(MnO_2)_y(H_2O)_z \rightleftharpoons x\ MnO + y\ MnO_2 + z\ H_2O$$

The proponents of this concept also suggest that this reaction may be reversible.

Nichols and Walton (33) showed that when manganous hydroxide was oxidized by oxygen in a basic medium, complete oxidation to the dioxide state was not possible under their experimental conditions. They found that the final volume of oxygen absorbed varied from 67 to 83 percent of the volume theoretically required for the formation of manganese dioxide. Meyer and Nerlich (31) found in their work that the volume of oxygen absorbed varied between 81 and 94 percent of the amount corresponding to the formation of manganese dioxide. Herman and Lievin (11) were unable to observe an absorption of more than 82 percent of the theoretical volume of oxygen necessary for the formation of manganese dioxide. Nichols and Walton concluded that the higher oxides of manganese exist in the following forms:

$$Mn_3O_4,\ Mn_2O_3,\ MnO_2$$

Naftel (32) showed that Mn_2O_3 exists in the soil. If these compounds are put in a form comparable to the form that is used by the writer of this paper, the oxides would take the following forms:

$$(MnO)_2(MnO_2),\ (MnO)\ (MnO_2),\ MnO_2$$

In their explanation of the mechanism of the reactions, Nichols and Walton (33) presented two possible ways in which the reactions could take place. One of the mechanisms would entail a step by step reaction, in which the manganese would be oxidized to the next higher state of oxidation to the next and so on. The following chemical equations illustrate the various reactions:

$$6\ Mn(OH)_2 + O_2 \rightleftharpoons 2\ Mn_3O_4 + 6\ H_2O$$

$$4\ Mn_3O_4 + O_2 \rightleftharpoons 6\ Mn_2O_3$$

$$2\ Mn_2O_3 + O_2 \rightleftharpoons 4\ MnO_2$$

The second mechanism shows that a certain portion of the manganese is oxidized to the dioxide form, followed by the formation of addition-like compounds without any further oxidation.

$$2\ Mn(OH)_2 + O_2 \rightleftharpoons MnO_2 + 2\ H_2O$$

$$4\ MnO_2 + Mn^{++}\ H_2O \rightleftharpoons Mn_2O_3 + 2\ H^+$$

$$2\ Mn_2O_3 + Mn^{++}\ H_2O \rightleftharpoons Mn_3O_4 + 2\ H^+$$

Nichols and Walton are inclined to feel that the second mechanism explains their experimental results more adequately than the first. If the second mechanism of reaction is assumed as the correct reaction, then there is some confirmatory evidence supporting the concept introduced by Fujimot and Sherman (6). This can be visualized more clearly if the equations of the reactions are modified and only oxygen and manganous hydroxide are used as the reactants, instead of the usage of the manganous ion and water in addition to the other reactants.

$$2\,Mn(OH)_2 + O_2 \rightleftharpoons MnO_2 + H_2O$$

$$MnO_2 + Mn(OH)_2 \rightleftharpoons (MnO)(MnO_2)(H_2O)$$

$$(MnO)(MnO_2)(H_2O) + Mn(OH)_2 \rightleftharpoons (MnO)_2(MnO_2)(H_2O)_2$$

The products of the second and third chemical equations approximate the hydrated oxide of Fujimoto and Sherman, with the exception that the subscripts are definite numbers.

Judging from all the observable data, there apparently exist three basic forms of manganese in the soil from the standpoint of availability to the plant. The manganous ion or the manganous oxide is readily available to plants. The hydrated form is not readily available but becomes available with changes in physical conditions in the soil, especially changes in temperature and water content. The third is the difficultly available form, the manganese dioxide, which becomes available only after drastic changes in the soil. The relationship between the three forms can be shown in the following representation:

$$MnO \rightleftharpoons (MnO)_x(MnO_2)_y(H_2O)_z \rightleftharpoons MnO_2$$

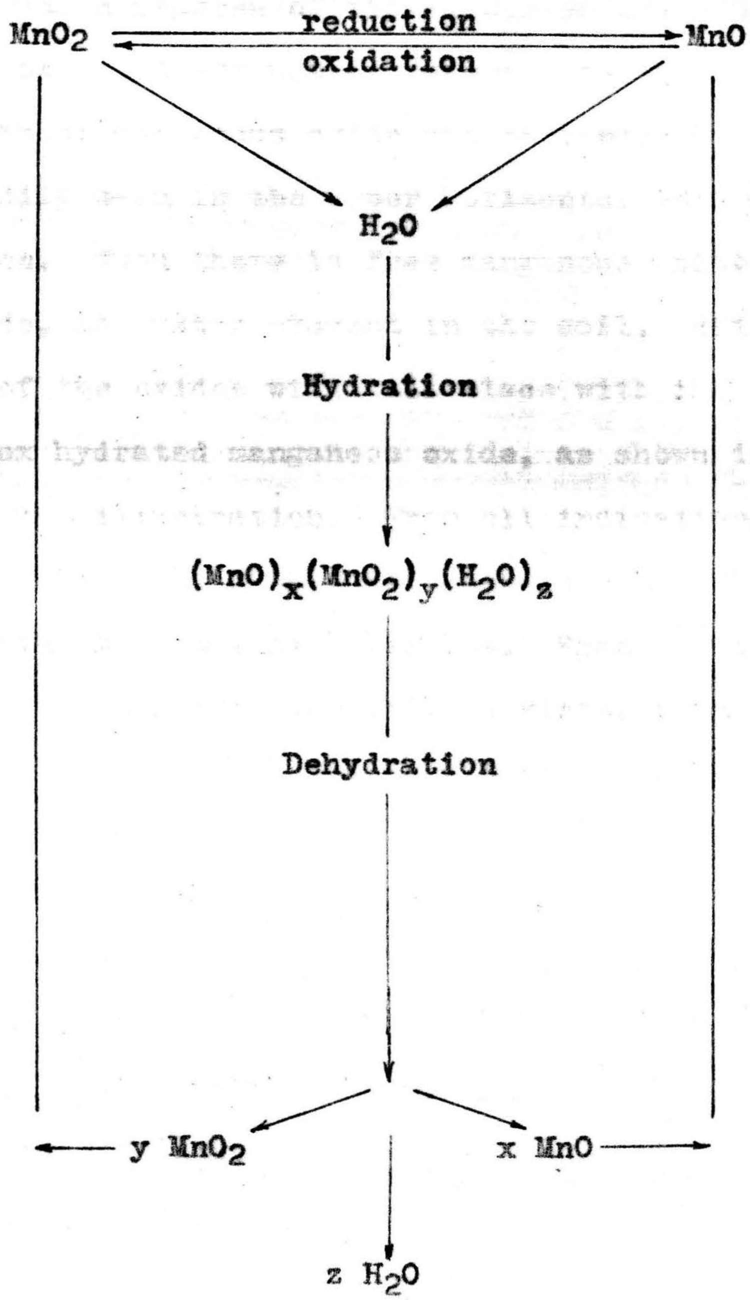
Leeper (21) proposed a similar relationship based upon the degree of reactivity to certain mild reducing agents. He classified the manganese into the manganous manganese, the colloidal hydrated manganese dioxide, which is easily reducible, and the inert manganese dioxide. He has suggested a new hypothesis in which the various forms of soil manganese would exist in an equilibrium which can be expressed by the following equation:

$$\text{Manganous manganese} \rightleftharpoons \text{Colloidal hydrated } MnO_2 \rightleftharpoons \text{Inert } MnO_2$$

This relationship is essentially similar to the relationship proposed by the author. The only difference between the two is the state of oxidation of the hydrated form as proposed by this writer and the state of oxidation of Leeper's colloidal hydrated manganese dioxide. In a later paper, Leeper (23) speaks of the manganic oxides or the higher oxides which include Mn_2O_3, Mn_3O_4, and MnO_2. He states that a certain portion of the manganic oxide is easily reducible and the rest of the manganic oxide is inert. With the recent modification introducted by Leeper, there seems to be no essential difference between the two propositions, except that both are set up on different criteria.

With the foregoing considerations, it seems possible now to introduce a new hypothesis on the manganese cycle in the soil. The following figure (Figure I) is a graphic representation of the writer's concept of the actual behavior of the various forms of manganese in the soil.

Figure I. The manganese cycle in soil



In the soil, there are two processes in motion which influence the availability of manganese. The first is the oxidation-reduction process, and the second is the hydration-dehydration process of the manganese oxide in the soil. The oxidation-reduction system determines the relative amounts of manganous oxide and manganese dioxide. This can be readily seen in the upper horizontal part of the illustration. When there is free manganous oxide, manganese dioxide, and water present in the soil, addition and hydration of the oxides will take place with the formation of a complex hydrated manganese oxide, as shown in the lower portion of the illustration. From all indications, this form of oxide is stable when moisture is present in the soil and when the temperature is low. When the soil becomes dry and the soil temperature rises, this form of oxide breaks up into its component parts. The component parts can then come under the influence of either one of the two processes, or one of the components (manganous oxide) may be taken up by plants. In this way is the manganese cycle in the soil realized.

The manganese cycle as illustrated can be utilized for the purpose of understanding how to influence the manganese status in soils. The point where control can be most effectively used is at the oxidation-reduction portion. In Hawaii, because of the high manganese content in the soil, the aim would naturally be to reduce the availability of manganese. This can be done by bringing about conditions that would allow the oxidation of manganese to take place more readily. To do this lime, dolomite, or any other soil treatment that would raise the pH of the soil can be added. On the other hand, acid forming substances and reducing agents should not be applied to manganiferous soils. Organic matter, especially those with a high carbon-nitrogen ratio, should not be applied and intimately mixed with the soil. If reducing agents are kept out of the soil, and the pH of the soil is raised, the manganous form of manganese will rapidly be oxidized to the dioxide form in which form it is not available to plants. At the same time any manganous oxide, released by the dehydration of the complex hydrated oxide, will be oxidized to the dioxide form. In this way even the potentially available form (hydrated oxide) will be reduced in the soil.

There is another point at which control of the availability of manganese can be exercised. This can be done by influencing the hydration or dehydration of the manganese oxides. In the field, rainfall and temperature cannot be controlled. However, the degree of wetness and the soil temperature can be influenced to a certain extent. Surface mulching will influence the soil temperature and the rate of evaporation of moisture from the soil. Irrigation also will change the moisture relations in the soil. When the soil is kept moist and cool, hydration of the manganese oxide will take place. This will lead to a lower availability of manganese.

In agricultural practices, complete control of the availability of manganese cannot be expected. However, the judicious use of the hypothesis of the manganese cycle in soils and the methods of influencing the manganese cycle may prove highly profitable.

SUMMARY

A study was made of the effect of various chemical treatments upon the fixation and release of manganese in Hawaiian soils. The results may be summarized as follows:

1. Application of lime and dolomite resulted in the fixation of manganese in the soil. Plant uptake of manganese was decreased by the treatment of soil with lime or dolomite.
2. Sulfur, when applied to soils, increased the exchangeable manganese, and increased the absorption of manganese by plants.
3. Addition of organic matter (sugar, sugar cane leaves, and pineapple leaves) to the soil resulted in an increase in exchangeable manganese and plant absorption of manganese.
4. Chemical reducing agents increased the level of exchangeable and hydrated forms of manganese.
5. A new hypothesis on the manganese cycle in soils

is presented. The manganese cycle is based upon the oxidation-reduction system and the hydration-dehydration system in soils.

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